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Facile fabrication of robust TiO_2@SnO_2@C hollow nanobelts for outstanding lithium storage

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HIGHLIGHTS

- A unique TiO_2@SnO_2@C hollow nanobelts had been facilely fabricated for the first time.
- The possible formation mechanism of this nanostructure had been proposed.
- The as-fabricated nanostructure endowed this composite with robust stability.
- This composite exhibited high capacity and long cycling life.

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ABSTRACT

Elaborate fabrication of state-of-the-art nanostructure SnO_2@C-based composites greatly contributes to alleviate the huge volume expansion issue of the SnO_2 anodes. But the preparation processes of most of them are complicated and tedious, which is generally adverse to the development of SnO_2@C-based composite anodes. Herein, a unique nanostructure of TiO_2@SnO_2@C hollow nanobelts (TiO_2@SnO_2@C HNBs), including the characteristics of one-dimensional architecture, sandwich protection, hollow structure, carbon coating, and a mechanically robust TiO_2 support, has been fabricated by a facile approach for the first time. As anodes for lithium-ion batteries, the as-fabricated TiO_2@SnO_2@C HNBs exhibit an outstanding lithium storage performance, delivering capacity of 804.6 and 384. 5 mAh g^{-1} at 200 and even 1000 mA g^{-1} after 500 cycles, respectively. It is demonstrated that thus outstanding performance is mainly attributed to the unique nanostructure of TiO_2@SnO_2@C HNBs.

1. Introduction

In the case of anodes for lithium-ion batteries (LIBs), the research mainly focuses on the development and search new promising materials to replace the currently dominated graphite anodes to service the next generation advanced LIBs. With high theoretical capacity of 782 mAh g^{-1} and appropriate working potential (average 0.5 V *vs.* Li/Li^+), SnO_2 has been considered to be one of the most promising anodes for next generation advanced LIBs, and hence attracted extensive attention [1–5]. But, the severe issues of poor conductivity and especial structure deterioration originated from huge volume variation (300%, mainly between 0.01 and 2.0 V) during lithiation/delithiation process cause a failure of cycle stability [6,7]. In order to improve the cycle stability, great efforts have been made to maintain the structure integrity from the volume variation. Currently, one of the common strategies is to design and fabricate nanostructures of SnO_2/C composites, because they have two key advantages: One is the nanometer-sized structure can effectively reduce the absolute volume change of SnO_2 and shorten the diffusion distance for ions and electrons; Other one is the carbon component with flexible and conductive natures can not only buffer the volume change of SnO_2 to a certain content, but also improve the conductivity of integral active materials, ultimately resulting in improved capacity retention cycle stability [8–12]. Especially the SnO_2/C composites with hollow nanostructures have attracted great attention in lithium-ion battery anode material field due to their inherent advantages: The inner cavity of hollow structures can offer a larger free space for accommodating the huge volume change of SnO_2 and releasing the mechanical strain generated during repeated volume

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expansion/contraction process; The larger specific surface area and shells of the hollow structures can ensure a high contact interface between the active materials and the electrolyte and a shortened diffusion distance for electrons and ions in spherical radial directions (namely vertical shells), respectively [5].

In addition, it is suggested that introduction of TiO_2 into SnO_2/C composites can further reinforce the mechanical stability of SnO_2/C composites, because the TiO_2, known for its superior stability (4% volume expansion), can act as a robust structure support for protecting the SnO_2/C composites. Thus, many works about TiO_2/SnO_2/C or TiO_2@SnO_2 composites have been reported, and showed better cycle stability than that of SnO_2/C or SnO_2 counterparts. Kim et al. fabricated heterostructured TiO_2/SnO_2 nanotube (NT) arrays by template-assisted atomic-layer deposition (ALD), where the TiO_2 and SnO_2 was located at the outer and inner shell of nanotubes, respectively; The structure stability of SnO_2 was improved by the synergistic effect between hollow nanotube arrays and TiO_2 confine [13]. Hou et al. prepared a hybrid of TiO_2 nanorods coating SnO_2 nanoparticles grown on carbon cloth; This hybridization strategy effectively enhanced the structure stability and conductivity of SnO_2 anode materials [14]. Yang et al. encapsulated the TiO_2/SnO_2 dual-phase nanoparticles into nanofibers to form an interesting one-dimensional composite; The TiO_2 phase and nanofiber encapsulation suppressed the pulverization and aggregation of SnO_2 nanoparticles and promoted the lithium storage and cycling performance of the SnO_2 anode-based cells [15]. Jeun et al. synthesized SnO_2@TiO_2 double-shell nanotubes by facile atomic layer deposition (ALD) using electrospun PAN nanofibers as templates; The synergistic effect between hollow space and TiO_2 confine greatly reinforced the structure stability of SnO_2 [16]. Wang et al. suggested that composite with TiO_2 can effectively improve the structure stability of SnO_2 anodes by restraining the huge volume change of SnO_2 in their Review [17]. Xie et al. developed a self-templated strategy to fabricate hierarchical TiO_2/SnO_2 hollow spheres coated with graphitized carbon (HTSO/GC-HSs) by combined sol-gel processes with hydrothermal treatment and calcinations; The as-prepared mesoporous HTSO/GC-HSs presented an approximate yolk-double-shell structure, with high specific area and small nanocrystals of TiO_2 and SnO_2; The shells composed of small nanocrystals of TiO_2 and SnO_2 coated with graphitized carbon; This hybrid structure endowed the SnO_2 anode-based cells with superior electrochemical reactivity and stability [18]. Madian et al. anodically fabricated TiO_2/SnO_2 nanotubes, the one-dimensional hollow structure and TiO_2 support effectively enhanced the cycling stability of SnO_2 anodes [19] [20]. Li et al. designed a low cost, up-scalable and one-pot wet-mechanochemical approach to fabricate TiO_2/SnO_2@graphene nanocomposites where TiO_2 and SnO_2 solid solution nanoparticles are evenly anchored on graphene sheets; The excellent conductivity of 3D porous graphene networks and structural stability of TiO_2 support provided this SnO_2 anode-based cells with superior rate capability and outstanding reversible cycling stability by synergistic effects [20]. But, the specific capacities calculated based on the mass of TiO_2/SnO_2/C composites are hardly satisfactory due to the lower practical theoretical capacity of TiO_2 (168 mAh g^{-1} for anatase TiO_2) which will pull down the overall capacities. It is proposed that the overall performance of TiO_2/SnO_2/C composites including specific capacity, rate capability and cycle life can be further improved via the optimization and improvement of structures or component proportions of TiO_2/SnO_2/C composites.

Herein, a novel nanostructure of TiO_2@SnO_2@C hollow nanobelts (TiO_2@SnO_2@C HNBs) has been facilely fabricated by a well-designed facile for the first time, as shown in Fig. 1. In the TiO_2@SnO_2@C HNBs, the distribution of SnO_2 is belt-likely tubular and sandwiched inner TiO_2 and outer carbon coating. Moreover, it is worthy of noting that unlike the general strategies involved templates for preparing complex TiO_2@SnO_2@C nanomaterials which need to orderly undergo SnO_2 coating, polysaccharides coating, TiO_2 coating and template removal tedious preparation process, our strategy creatively realized the simultaneous achievement of SnO_2 coating, polysaccharides coating, template removal and formation of TiO_2 support during hydrothermal treatment process, exhibiting greatly simplified peculiarity. Thus, the TiO_2@SnO_2@C HNBs fully combine all the characteristics of one-dimensional architecture, sandwich protection, hollow structure, carbon coating, and a mechanically robust TiO_2 support in particular, ultimately resulting in an outstanding lithium storage performance in terms of high capacity and long cycling life. And, this strategy may offer a broader vision into facile preparation of one-dimensional complex multi-shelled hollow transition metal oxide nanomaterials for application in other hot fields such as dye-sensitized solar cells, supercapacitors, catalysis, drug delivery, sensors and so on.

2. Experimental section

2.1. Preparation of TiO_2@SnO_2@C HNBs

All chemicals (analytical grade) were purchased from Shanghai Aladdin biochemical technology co., LTD and used without further purification. Typically, 1 ml of tetrabutyl titanate was dropwise added into 20 ml of 10 M NaOH aqueous solution under constant stirring. After stirring for 30 min, the achieved white suspension was transferred into a stainless steel autoclave with Teflon-lining and carefully placed in an oven at 180 °C for 24 h. After the end of the first hydrothermal treatment, the obtained white precipitate (sodium titanate) was collected by centrifugation, washed with deionized water and ethanol thoroughly. Then, re-dispersion of the collected precipitate into 100 ml of 0.1 M HCl and stirring over night to prepare hydrogen titanate ($H_2Ti_3O_7$) nanobelts (HTO NBs). 100 mg of as-prepared dry HTO NBs was dispersed into 140 ml solution composed of deionized water and ethanol (1:1 by volume) containing 400 mg of cetyl trimethyl ammonium bromide (CTAB) in advance by ultrasound for 1 h, then addition of 1.5 ml of concentrated ammonia solution (25-28 wt.%) and stirring for another 1 h. After that, 0.2 ml of tetraethyl orthosilicate (TEOS) was added into above suspension drop by drop under stirring. After stirring for 6 h, the white HTO NBs@SiO_2 composite was collected using the same process with the HTO NBs, and then dried at 60 °C overnight. For preparation process of TiO_2@SnO_2@C HNBs, dispersion of 100 mg of as-prepared HTO NBs@SiO_2 into 60 ml deionized water via ultrasound for 20 min to form a suspension. 1.2 g of glucose was added into the suspension and stirred for 10 min. After that, addition of 0.2 g of tin (II) chloride dehydrate ($SnCl_2{\cdot}2H_2O$) and 0.044 g of ammonium fluoride (NH_4F) into the mixed suspension with 30 min interval and then continuous stirring another 30 min. Then, transfer this mixed suspension into a Teflon-lined stainless steel autoclave, and carefully placed in an oven heated to 180 °C in advance for 24 h. After end of the finally hydrothermal treatment, the generated dark brown precipitate was collected by centrifugation, washed with deionized water and ethanol thoroughly, and dried at 60 °C. After final carbonization of the obtained dark brown precipitate at a temperature of 500 °C for 3 h with a ramping rate of 0.5 °C min^{-1} under argon atmosphere, the TiO_2@SnO_2@C HNBs was obtained.

2.2. Materials characterizations

The morphology and microstructure studies of TiO_2@SnO_2@C HNBs were conducted by using transmission electron microscopy (TEM, JEOL JEM-2010) and field emission scanning electron microscopy (FE-SEM, JEOL JSM-7401F) with an energy dispersive X-ray spectrometer (EDX). The X-ray diffraction (XRD, Rigaku, Cu K X-ray radiation), X-ray photoelectron spectroscopy (XPS, K-Alpha) and Raman spectroscopy (Bruker, Senterra R200-L dispersive Raman microscope) techniques were applied to investigate the crystal structure and composition natures of TiO_2@SnO_2@C HNBs composite. The thermogravimetric analysis instrument (TGA, SDT Q600 V8.2 Build 100) was employed to demonstrate the carbon content of TiO_2@SnO_2@C HNBs composite.